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Express Mail No. EV041916131US

What is claimed is:

1. A method of determining a test concentration of conductive species in an aqueous system, comprising:
 - determining a relationship between cell resistance of an electrochemical cell and concentration of conductive species;
 - measuring an electrochemical parameter of the electrochemical cell; and
 - determining the test concentration of conductive species based upon the relationship and the electrochemical parameter.
2. The method of claim 1, wherein the conductive species comprise one or more chemical constituents selected from the group consisting of metal ions, hydrogen ions, and hydroxyl ions.
3. The method of claim 1, wherein determining the relationship comprises:
 - (a) providing a first concentration of conductive species;
 - (b) measuring at least one electrochemical parameter of the electrochemical cell;
 - (c) providing a second concentration of conductive species different than the first concentration of conductive species; and then
 - (d) measuring the at least one electrochemical parameter of the electrochemical cell.
4. The method of claim 3, further comprising:
providing additional concentrations of conductive species, substantially different from the first concentration and the second concentration and different from one another, and then measuring the at least one electrochemical parameter of the electrochemical cell.

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5. The method of claim 3, further comprising:
adjusting a process variable; and
repeating (b), (c), and (d) in sequence at least one time.
6. The method of claim 3, wherein the test concentration has a numerical value that is between the first concentration and the second concentration.
7. The method of claim 4, wherein the test concentration has a numerical value that falls in a numerical range defined by a largest and a smallest of the group consisting of the first concentration, the second concentration, and the additional concentrations.
8. The method of claim 1, wherein the one or more electrochemical parameters comprise a cell voltage.
9. The method of claim 3, wherein (c) comprises adding conductive species to the electrochemical cell.
10. The method of claim 1, wherein the electrochemical cell has a series resistance which is less than the cell resistance.
11. The method of claim 1, wherein the electrochemical cell has an electrical conductivity between about 40 milisiemens/cm² and about 1000 milisiemens/cm².
12. A method of determining whether an aqueous system has a concentration of conductive species within a specified range, comprising:
providing an electrochemical cell containing the aqueous system wherein the electrochemical cell has a cell resistance that varies with a concentration of conductive species;
determining a relationship between the cell resistance of the electrochemical cell and the concentration of conductive species;

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measuring one or more electrochemical parameters of the electrochemical cell;

determining a test concentration of conductive species based upon the relationship and the one or more electrochemical parameters; and

concluding the test concentration is within a specified range when the test concentration is less than a pre-determined maximum concentration and more than a predetermined minimum concentration.

13. The method of claim 12, wherein the conductive species comprise one or more chemical constituents selected from the group of metal ions, hydrogen ions, and hydroxyl ions.

14. The method of claim 12, wherein the determining of the relationship between the cell resistance and the concentration of conductive species further comprises:

- (a) providing a first concentration of conductive species;
- (b) measuring at least one electrochemical parameter of the electrochemical cell;
- (c) providing a second concentration of conductive species different than the first concentration of conductive species; and then
- (d) measuring the at least one electrochemical parameter of the electrochemical cell.

15. The method of claim 14, further comprising:

providing additional concentrations of conductive species, substantially different from the first concentration and the second concentration and different from one another, and then measuring the one or more electrochemical parameters of the electrochemical cell.

16. The method of claim 14, further comprising:

- adjusting a process variable; and
- repeating (b), (c), and (d) in sequence at least once.

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17. The method of claim 14, wherein the test concentration has a numerical value that is between the first concentration and the second concentration.
18. The method of claim 15, wherein the test concentration has a numerical value that falls in a numerical range defined by the largest and smallest of the first concentration, the second concentration, and the additional concentrations.
19. The method of claim 12, wherein the one or more electrochemical parameters comprise a cell voltage.
20. The method of claim 14, wherein (c) comprises adding conductive species to the electrochemical cell.
21. The method of claim 12, wherein the electrochemical cell has an electrical conductivity between about 40 milisiemens/cm² and about 1000 milisiemens/cm².
22. A method of measuring a concentration of conductive species in an electrochemical plating bath contained in an electroplating cell having an anode and a cathode, comprising:
- determining a relationship between cell resistance of the electrochemical cell and the concentration of conductive species;
 - beginning an electroplating operation by electrically biasing the anode and the cathode;
 - during the electroplating operation, measuring an electrochemical parameter of the electrochemical cell; and
 - determining the concentration of conductive species based upon the determined relationship and the electrochemical parameter.
23. The method of claim 22, wherein the electrochemical parameter is measured continuously during the electroplating operation.

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24. The method of claim 23, wherein the electrochemical plating bath flows continuously through the electrochemical cell, and the concentration of conductive species is continuously measured.
25. The method of claim 24, wherein additional conductive species are added to the electrochemical plating bath at a rate responsive to changes in the concentration measurements.
26. The method of claim 22, wherein the conductive species comprise one or more chemical constituents selected from the group consisting of metal ions, hydrogen ions, and hydroxyl ions.
27. The method of claim 22, wherein determining the relationship between the cell resistance and concentration of conductive species comprises:
- (a) providing a first concentration of conductive species;
 - (b) measuring at least one electrochemical parameter of the electrochemical cell;
 - (c) providing a second concentration of conductive species different than the first concentration of conductive species; and then
 - (d) measuring the at least one electrochemical parameter of the electrochemical cell.
28. The method of claim 27, further comprising:
providing additional concentrations of conductive species, substantially different from the first concentration and the second concentration and different from one another, and then measuring the one or more electrochemical parameters of the electrochemical cell.
29. The method of claim 27, further comprising:
adjusting a process variable; and
repeating (b), (c), and (d) in sequence at least one time.

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30. The method of claim 22, wherein the one or more electrochemical parameters comprise a cell voltage.
31. The method of claim 27, wherein (c) comprises adding conductive species to the electrochemical cell.
32. The method of claim 22, wherein the electrochemical cell has an electrical conductivity between about 40 milisiemens/cm² and about 1000 milisiemens/cm².
33. The method of claim 22, wherein the anode has an anode cross-sectional area and the cathode has a cathode cross-sectional area, and the cross-sectional area of the anode is within a range of about 85% to about 115% of the cross-sectional area of the cathode.
34. The method of claim 22, wherein the cathode comprises a semiconductor wafer having a metal layer formed thereon.
35. The method of claim 29, wherein the process variable is a cell current.
36. The method of claim 29, wherein the anode comprises copper.
37. A system for electroplating a material layer on a substrate, comprising:
an electroplating apparatus for electroplating a material layer on a substrate, the electroplating apparatus comprising:
an electroplating bath;
an electrochemical sensing device capable of measuring a cell resistance of the electroplating bath; and
one or more material storage reservoirs capable of delivering one or more materials to the electroplating bath in order to adjust a concentration of conductive species therein.

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38. The system of claim 37, further comprising a controller coupled to the electroplating bath and the electrochemical sensing device to effectuate changes in the cell resistance of the electroplating bath.
39. The system of claim 38, further comprising a processor coupled to the controller to determine a desired concentration of conductive species based upon the cell resistance sensed and to provide control information indicative of the desired concentration of conductive species to the controller, and the material storage reservoirs are coupled to the controller.
40. The system of claim 39, wherein the controller and processor are operable to control the flow rate of conductive species from the sources to the electroplating bath in response to the concentration information supplied by the controller.
41. The system of claim 40, wherein the controller is adapted to continuously supply information to the controller concerning the concentration of conductive species in the electroplating bath the processor is adapted to continuously determine the amount of conductive species to be introduced into the electroplating bath and continuously provide information on the determined amount to the controller, and the controller is adapted to effectuate an appropriate flow rate of conductive species from the source to the electroplating bath.
42. A system as defined by claim 37, wherein the electroplating apparatus includes an anode and a cathode and the electrochemical sensing device is connected to the anode and the cathode.
43. A method for continuously controlling the acidity of an electroplating bath in an electrochemical cell during an electroplating operation, comprising:
- determining the relationship between concentration of acid in the bath and resistance of the electrochemical cell;
 - continuously monitoring the resistance of the electrochemical cell;

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based on the relationship and the resistance, continuously providing a signal indicative of the concentration of acid in the bath to a controller; and

controlling the addition of acid to the bath in response to the provided signals to provide real time adjustment of the concentration of acid.

44. The method of claim 43, wherein the relationship of the concentration of acid to the resistance of the electrochemical cell is determined by:

providing a first concentration of conductive species;

measuring at least one electrochemical parameter of the electrochemical cell;

providing a second concentration of conductive species different than the first concentration of conductive species; and

measuring the at least one electrochemical parameter of the electrochemical cell.

45. A method for determining the concentration of a conductive species in an electrochemical cell, comprising:

determining the relationship between the resistance of the electrochemical cell and the concentration of the conductive species by:

(a) providing a liquid containing a known concentration of conductive species;

(b) establishing an electrical circuit including an anode and a cathode in the liquid and a measuring device selected from the group consisting of a voltmeter and an ammeter;

(c) passing an electrical current of known voltage or current through the circuit;

(d) calculating the resistance of the liquid by applying Ohm's Law; and

(e) repeating (a) – (d) one or more times with liquid having a different known concentration of the conductive species until the relationship is determined;

providing a test liquid system containing an unknown concentration of a conductive liquid species;

repeating (b) and (c) with the test liquid;

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measuring the voltage or amperage in the circuit; and
determining from the relationship and the voltage or amperage the
concentration of conductive species in the test liquid.

46. The method of claim 45, wherein the measuring the voltage is continuous
during at least a part of an electroplating operation and the concentration of the
conductive species is continuously determined during at least a part of the
measuring the voltage.

47. The method of claim 46, wherein the concentration of the conductive
species is continuously modified in response to the determining from the
relationship.

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